PATENT SPECIFICATION 1,158,924

DRAWINGS ATTACHED.

1,158,924

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COMPLETE SPECIFICATION.

Improvements in and relating to Methods of Manufacturing Devices Comprising a Layer of Grains.

We, PHILIPS ELECTRONIC AND ASSOCIATED INDUSTRIES LIMITED, of Abacus House, 33 Gutter Lane, London, E.C.2, a British Company, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The invention relates to methods of manufacturing devices comprising a layer of grains, particularly but not exclusively devices in which the layer has the thickness of one grain, the grains cohering by means of a binder, surface parts of the grains on at least one side of the layer of grains being free from the binder and provided with an electrode, and further relates to devices, for example, semiconductor devices, when manufactured by such methods. For semiconductor devices grains may be used which consist wholly or partly of semiconductor material.

The devices may be constructed for operation, *inter alia*, as detectors for either corpuscular or electromagnetic radiation, for instance photo-diodes and photo-resistors in which radiation energy impinges on a photosensitive layer and produces therein electric voltage differences or impedance variations which are detected by means of electrodes arranged on the layer. Similar devices may also be constructed for the conversion of radiation energy into electric energy, *inter alia* as so-called solar batteries.

Another field of application for the devices is the conversion of electric energy into radiation energy as may be effected, for example, by recombination radiation in p-n junctions in semiconductors, by electroluminescence, and so on.

As described in our Copending Patent Application No. 34353/66 (Serial No. 1,158,922), layers of grains of substantially one grain thickness may advantageously be used in all these cases, since contact resistances between the individual grains are avoided and, in addition, the efficiency—owing to the absence of grains screened against radiation wholly or partly by other grains—and also the ratio (weight and material consumption)/active surface are as favourable as possible.

Both in this case and in cases in which the layer thickness is larger, for example, is several grain diameters, in order to obtain the thin layers of grains it is preferred to provide the grains and the binder on the support, which gives mechanical rigidity during the various processes.

In many cases it is desired to provide on the layer of grains an electrode layer which is in electric contact with the grains on the side of the layer adjacent the support. This may be effected, for example, by using a support which is electrically conductive at least over that part of its surface which is to be covered with the layer of grains. It is essential in this connection that on the side of the support the surface of the grains is at least partly free from the binder. In practice this condition can only be realized with difficulty, owing to the fact that a film of the binder can easily be formed between the support and the grains which film is difficult to remove and may cause the occurrence of a high and/or unstable contact resistance.

According to the invention, in a method of manufacturing a device comprising a layer of grains cohering by means of a binder, surface parts of the grains on at least one side of the layer of grains being free from the binder and provided with an electrode, a liquid adhesive layer is provided on a support

in which layer grains are sunk over part of their diameter, a binder is provided between the grains and hardened, the layer of grains with the binder is detached from the support by selectively removing the adhesive layer, and an electrode is provided on surface parts of the grains exposed on removal of the adhesive layer.

An advantage of this method is that two process steps necessary for providing a satisfactory contact to the grains are carried out in one operation, namely the detaching of the layer of grains from the support and the releasing of parts of the grains from the binder on the side of the layer adjacent the support. An electrode layer subsequently provided on the so exposed surface parts of the grains may form a stable contact with low contact resistance

In a preferred form of the method the layer of grains has substantially the thickness of one grain. As regards the materials to be used for the adhesive layer and the binder, a great variety of materials or material combinations may be chosen. In this connection it is to be noted that no stringent requirements are imposed upon the adhesive force of the adhesive layer. It is sufficient that the grains are temporarily held in place by the adhesive layer and are not detached from the adhesive layer when the binder is provided. As regards the properties and the material, the adhesive layer may be of a divergent nature. For example, a liquid or a viscous adhesive layer may be used on which a binder is provided. A hardenable adhesive layer may be used, the adhesive layer being hardened before the binder is provided. Hardening of the adhesive layer is to be understood to mean in this connection that the adhesive layer hardens to a hardness or viscosity which is greater than that of the binder in the non-hardened condition. As a result of this the binder when provided in the liquid condition does not displace the adhesive layer. Hardening may be effected by, for example, polymerisation, polycondensation or evaporation of a solvent.

The selective removal of the adhesive layer may be effected, for example, by using a readily volatilizable adhesive layer or an adhesive layer which is soluble selectively in suitable solvents, for example, a water-soluble adhesive layer. The adhesive layer may be provided in the form of a gel. Such a gel is built up from a liquid-containing skeleton of the gelated substance. The use of a gel as the adhesive layer thus has the advantage that liquid from the adhesive layer which by the capillary action might creep over the parts of the grains projecting above the adhesive layer, is substantially free from the gelated substance and leaves substantially no residues on the parts of the grains during evaporation. As a result of this the binder can afterwards adhere better to the surface of the grains which increases the coherence of the layer of grains. For such a gel may be used, for example, a polysaccharide having a high molecular weight gelated in water, such as starch or gum arabic.

Gelatin is a suitable gel for the method according to the invention. Gelatin can be provided in a simple manner on a support in a homogeneous layer and is easy to remove with warm water.

To give easier handling of the layer of grains with the binder when detached from the support, the side of the layer of grains remote from the support may be coated with a flexible layer of a synthetic material which is hardened before the adhesive layer is selectively removed. This layer of synthetic material may remain connected permanently to the layer of grains as a support, or may connect the layer of grains, if desired, with a permanent supporting member. If the layer of grains is to be provided with an electrode layer on the side of such a permanent layer of synthetic material, said electrode layer must be provided before the layer of synthetic material.

An adhesive layer may be provided, the thickness of which is less than half and preferably less than one fifth of the average diameter of the grains. This ensures that the grains remain projecting for the greater part above the adhesive layer so that they can better be embedded in the binder, which increases the rigidity. Moreover, the tops of the grains are approximately located in one plane as a result of which a regularly shaped layer is formed so that a more even contacting with an electrode layer can be obtained.

To accelerate the selective dissolving of the adhesive layer it is desirable that the layer of grains detaches from the support as rapidly as possible. For that purpose an intermediate layer may be provided on the support before providing the adhesive layer, this intermediate layer decreasing the adherence between the support and the adhesive layer and/or promoting the penetration of a solvent to be used between the adhesive layer and the support. The intermediate layer may consist, for example, of a surface-active substance which itself need not be soluble in the solvent to be used. As will be described later, an intermediate layer consisting of nitrocellulose may advantageously be used, in particular in combination with gelatin as an adhesive layer; also lecithin may be used as an intermediate layer, in combination with an adhesive layer containing saccharose and/or glucose.

The use of an adhesive layer is of particular advantage if grains are used consisting of a core of one material and an enveloping layer of another material.

In this case the core and the enveloping

layer may consist of different constituents, for example, different semiconductor materials. Alternatively, the core and the enveloping layer may be of the same main constituent, but as a result of a difference in doping have different conductivity properties. Of particular importance is, for example, the use of semiconductor grains the enveloping layer of which forms a p-n junction with the core. In one form of the method in accordance with the invention after hardening the adhesive layer and prior to applying the binder these grans are subjected to an etching treatment in which the enveloping layer is removed from the parts of the grains projecting above the adhesive layer and the parts of the grains sunk in the adhesive layer are protected by the adhesive layer against the action of the etchant. In this manner a layer of grains having the thickness of one grain is obtained, the adhesive layer containing only non-etched parts of the grains, and the binder being located on the etched parts of the grains.

After the selective removal of the adhesive layer, a layer of grains is obtained, in which on one side of the binder the remaining parts of the enveloping layer are accessible for contacting and in which on the side on the layer of grains remote from the support, parts of the grains associated with the core can be exposed through the binder, for example, by grinding. When electrode layers are provided on opposite sides of the layer of grains, there is no danger of short circuit of the core and the enveloping layer through one of the electrode layers.

Alternatively, instead of one support, as used in the preceding methods, two oppositely located supports may be used which are both provided with an adhesive layer. The advantage of this is that by applying the method in accordance with the invention in a similar manner to two sides of the layer of grains, a self-supporting layer of grains with binder is obtained, in which on both sides of the layer surface parts of the grains are contacted by an electrode

Embodiments of the invention will now be described, by way of two Examples, with reference to the accompanying diagrammatic drawings, in which:

Figure 1 is a sectional view of a part of a solar battery manufactured by a method in accordance with the invention;

Figures 2 to 4 are sectional views showing successive stages of manufacture of the solar battery shown in Figure 1; and

Figures 5 to 7 are sectional views showing successive stages of manufacture of another solar battery.

EXAMPLE I

In Figure 1 there is shown a solar battery comprising a layer of semiconductor grains 1 having the thickness of one grain of n-type cadmium sulphide. These grains have an average diameter of 30 microns and are held in the form of a layer by means of a binder 2. Surface parts 3 and 7 of the grains 1 on opposite sides of the layer of grains are not covered by the binder 2 and the surface parts 3 are coated by an electrode layer 10 which makes a substantially ohmic contact with the grains 1. The surface parts 7 are coated with a radiation-permeable electrode layer 8. which makes a rectifying contact with the grains 1. Radiation incident through the electrode layer 8 may cause a voltage difference across the said rectifying contact, which can be detected across the electrodes 8 and 10.

The method of forming the layer of grains will now be described and in this respect reference is invited to our Copending Patent Application No. 34354/66 (Serial No. 1,158,923). On a radiation-permeable support 4 (Figure 2) of glass, an intermediate layer 6 of nitrocellulose, a few microns thick, is first provided by dipping the support 4 in a solution of 10% nitrocellulose in butyl acetate and evaporating the solvent. An adhesive layer 5, approximately 5 microns thick, consisting of gelatin is then provided on the layer 6. This may be effected by dipping the support 4 in a solution of 15% gelatin in water at a temperature of approximately 40°C.

The cadmium sulphide grains 1 are then sunk in the said gelatin layer 5, which is still liquid, after which the gelatin layer 5 is dried and the grains not adhering to the layer 5 are removed. The layer of grains is then coated with a layer 2, 11 consisting of a photochemical substance which has the property of becoming insoluble in an appropriate developer by irradiation and remaining soluble in the non-irradiated position. Such substances are known under the name of negative photoresist. In this example a negative photoresist is used, which is commercially available as "Kodak (Registered Trade Mark) Photo Resist" (KPR). As described in the said Copending Patent Application, the layer 2, 11 is exposed through the support 4. The intensity of radiation and the duration of exposure are chosen to be so that the exposed photoresist parts 2 between the grains become insoluble whereas, as a result of the stronger radiation absorption in the grains 1, the parts 11 of the photoresist located above the grains and denoted in Figure 2 by broken lines, can be developed. By means of a developing process the photoresist parts 11 are removed and the parts 2 remain between the grains 1 as a binder.

The exposed surface parts 7 of the grains 1 are then coated (see Figure 3), by vapour deposition, with a transparent electrode layer 8 of copper of approximately 100 Å thickness.

The copper layer 8 forms a rectifying contact with the cadmium sulphide grains 1. For purposes of rigidity a radiation-transparent layer 9, of a hardenable synthetic material, for example, an epoxy resin with a thickness of approximately 200 microns, is then provided on said electrode layer 8, an area of the copper layer 8 being not coated for purposes of making an electrical contact (see Figure 1). After hardening the layer 9, the adhesive layer 5 of gelatin is removed by selective dissolving in water (see Figure 4). The gelatin layer 5 is easily detached from the intermediate nitrocellulose layer 6 and is then rapidly dissolved. Finally, an electrode layer 10 of indium is provided on the free surface parts 3 of the grains, for example, by vapour deposition (see Figure 1). This indium layer makes a substantially ohmic contact with the cadmium sulphide grains 1 and has a thickness of approximately 0·3 micron.

Instead of the gelatin layer 5 described other adhesive layers may be used. A water-soluble adhesive layer may be used consisting of a syrupy solution of one or more water-soluble saccharides, for example, a solution of 100 gm. of saccharose and 10 gm. of glucose in 50 ml. of water, to which solution approximately 0.3 gm. of a wetting agent on the basis of esterified sulphonated fatty acids may be added. The solution is provided on the support as a syrup, for example, by dipping, and is then dried. For facilitating the subsequent detaching from the layer of grains, the support may be coated with a thin layer of a surface-active substance, for example, lecithin.

EXAMPLE II

Semiconductor grains 21, 22 are used to form the layer which consists of a core 21 of n-type conductive material surrounded by an enveloping layer 22 of p-type material, a p-n junction 23 being present between the core 21 and the enveloping layer 22.

On a support 24 (Figure 5) a liquid adhesive layer 25 is provided. The grains 21, 22 are sunk in the layer 25 after which the layer 25 is hardened. The enveloping layer 22 is then etched away from the parts of the grains projecting above the adhesive layer (see Figure 6) so that surface parts 26 of the core 21 are obtained and the p-n junction 23 is also exposed at the surface. A binder 27 which can be hardened is then provided on the adhesive layer and the surface parts 26 of the grains. After hardening the binder 27 the adhesive layer 25 is removed by selective dissolution (Figure 7) as a result of which exposed surface parts 28 of the layer 22 are obtained at the side of the support. The p-n junction 23 remains covered by the binder 27. Then an electrode layer 29 is provided on the exposed surface parts 28 which makes a substantially ohmic contact with the surface parts 28. Exposed surface parts 30 of the core 21 are then obtained on the opposite side of the layer of grains, for example, by grinding away the binder 27. A second electrode layer 31 is then provided on the binder 27 and makes electrical contact with the surface parts 30.

When the electrode layer 29 is capable of passing solar radiation a solar battery is obtained in this manner in which radiation incident through the electrode layer 29 produces a voltage difference across the p-n junction 23 which can be derived from the electrode layers 29 and 31. In this manner also an electroluminescent panel may be formed in which the p-n junction 23 is biased in the forward direction by voltages applied to the electrode layers 29 and 31, and in which in the proximity of the junction 23 injection recombination radiation is produced which can emerge through the electrode layer 29.

In this Example grains of n-type CdTe surrounded by a p-type conductive layer 22 could be used which may be obtained by indiffusion of phosphorus according to methods commonly used in semiconductor technology. The material for the adhesive layer 25 may be polystyrene or polymethylmethacrylate which is soluble in aromatics such as benzene and toluene, while concentrated potassium hydroxide solution may be used as the etchant against which polystyrene and polymethylmethacrylate are resistant. An epoxy resin may be used as the binder 27 which is resistant to aromatic solvents, such as benzene and toluene.

Many further modifications are possible within the scope of the present invention as defined in the appended claims, for example many different materials may be used. The adhesive layer may be formed by many materials other than those mentioned herein as far as they are provided on a support in a liquid or syrupy condition and can be removed selectively by dissolving or in a different manner without the grains or the binder being attacked. In each individual case the expert will make the correct choice of materials matching one another in these respects.

WHAT WE CLAIM IS:—

1. A method of manufacturing a device comprising a layer of grains cohering by means of a binder, surface parts of the grains on at least one side of the layer of grains being free from the binder and provided with an electrode, in which a liquid adhesive layer is provided on a support in which layer grains are sunk over a part of their diameter, a binder is provided between the grains and hardened, the layer of grains with the binder is detached from the support by selectively removing the adhesive layer, and an electrode is provided on surface parts of the grains exposed on removal of the adhesive layer.

2. A method as claimed in Claim 1, in

which the layer of grains has substantially the thickness of one grain.

3. A method as claimed in Claim 1 or Claim 2, in which the adhesive layer is hardened before the binder is provided.

4. A method as claimed in any of Claims 1 to 3, in which the adhesive layer is a gel.

5. A method as claimed in Claim 4, in which the adhesive layer is gelatin.

6. A method as claimed in any of the preceding Claims, in which before providing the adhesive layer an intermediate layer is provided on the support, the intermediate layer decreasing the adherence between the support and the adhesive layer and/or promoting the penetration of the solvent to be used between the adhesive layer and the support.

7. A method as claimed in Claim 6 where appendant to Claim 5, in which the intermediate layer consists of nitrocellulose.

8. A method as claimed in Claim 6 where appendant to any of Claims 1 to 3, in which the intermediate layer consists of lecithin and the adhesive layer is provided by applying a solution containing saccharose and glucose in water onto the intermediate layer and subsequent drying the solution.

9. A method as claimed in any of the preceding Claims, in which the layer of grains with the binder is coated on the side remote from the support with a flexible layer of a synthetic material which is hardened before the adhesive layer is selectively removed.

10. A method as claimed in any of the preceding Claims, in which an adhesive layer is used the thickness of which is less than half of the average grain diameter.

11. A method as claimed in Claim 10, in which the thickness of the adhesive layer is less than one fifth of the average grain diameter.

12. A method as claimed in any of the preceding Claims, in which the grains consist of a core of one material and an enveloping layer of a different material and, after hardening the adhesive layer and prior to applying the binder, the grains are subjected to an etching treatment in which the enveloping layer is removed from the parts of the grains projecting above the adhesive layer and the parts of the grains sunk in the adhesive layer are protected by said adhesive layer against the action of the etchant.

13. A method as claimed in any of Claims 1 to 8 or in any of Claims 10 to 12 where appendant to any of Claims 1 to 8, in which a second support, also provided with an adhesive layer, is provided on the side of the layer of grains remote from the support.

14. A method of manufacturing a device comprising layer of grains substantially as herein described with reference to Figures 1 to 4 or Figures 5 to 7 of the accompanying drawings.

15. A device comprising layer of grains when manufactured by a method claimed in any of the preceding Claims.

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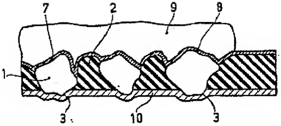

FIG.1

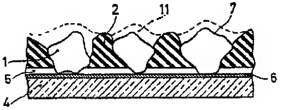

FIG.2

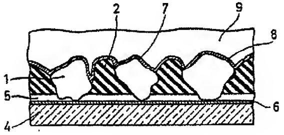

FIG.3

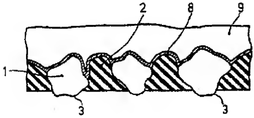

FIG.4

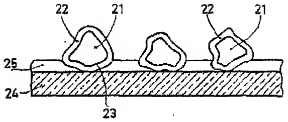

FIG.5

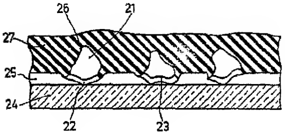

FIG.6

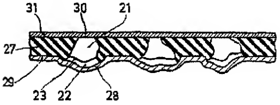

FIG.7